Production of O_2^+ following the double ionization of CO_2

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Synopsis Although CO_2 ionization and fragmentation have been the object of many studies, so far the production of O_2^+ had not been reported. In this work, absolute cross sections for the production of O_2^+ following ionization of CO_2 by electron impact is reported for the first time. We guarantee that the O_2^+ is produced by the CO_2 fragmentation by measuring its kinetic energy distribution with the DETOF technique.

The removal of one or more electrons from molecules opens up a myriad of post-collisional pathways for the system, either through stabilization of fragmentation. Furthermore, when a molecule is ionized, it is usually taken, along the Franck-Condon region, to an excited vibrational state of the new electronic configuration. This creates the possibility for new bonds to be formed between nuclei that were not originally bound to one another in the parent molecule. One such example is the well-known pathways leading to the formation of (vibrationally excited) H_2 in the fragmentation of the water molecule [1].

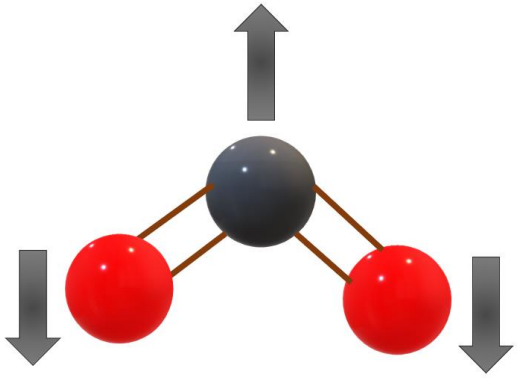

Figure 1. Illustration of the bending vibrational mode of the CO_2 molecule that leads, after the removal of two electrons, to the $C^+ + O_2^+$ fragments formation. Black and red represent the carbon and oxygen nuclei, respectively.

On the other hand, such a pathway has never been reported for carbon dioxide so far [2,3]. Differently from water, where the hydrogen nuclei stand at a ~104º angle with respect to the oxygen nucleus in the fundamental state of the molecule, carbon dioxide presents a linear structure. Nevertheless, there are well-know vibrational states of the molecule [4], including stretching and bending modes (see figure 1). In addition, the removal of more than one electron from a molecule has been shown to produce strong geometrical rearrangements in more complex compounds such as benzene [5], making it reasonable to expect that it can lead to moieties containing elements not originally bound.

The breakup of the CO_2 following ionization was studied by means of a pulsed electron gun in the 30 to 800 eV energy range, a gas cell with monitored pressure and a time-of-flight mass spectrometer. Along with all other known ionic fragments coming from CO_2 ionization [2,3], we report here the observation of the O_2^+ ion. The DETOF technique, which allows one to determine the kinetic energy distributions presents for each produced fragment [5], was employed to ascertain that the detected O_2^+ did not com from air contamination – if its parent molecule were O_2, then the resulting ion would have a Maxwell-Boltzmann thermal distribution, since it wouldn't have come from fragmentation and therefore would not acquire velocity, which happens in the breakup process. That was not the case here – the observed O_2^+ has a kinetic energy distribution centered at 1.4 eV for all measured impact energies above 40 eV.

References

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